Dephosphorization of Stainless Steels

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After briefly describing the importance of the dephosphorization of stainless steels from the viewpoint of their corrosion resistance, as well as their production methods, the physicochemical principles of dephosphorization by oxidation and reduction are presented in more detail.

When phosphorus is removed by oxidation, the oxidation loss of chromium has to be curtailed. The prevailing oxygen partial pressure is limited by the CaO-CaO.Cr₂O₃ equilibrium if CaO-bearing slags are used. Therefore, highly basic slags have been developed that can function effectively under relatively lower oxygen pressures. Some examples of their use are shown.

Dephosphorization under reducing conditions is a new concept and is effective for alloys containing a large amount of chromium. Test data on the use of Ca-CaF₂ and CaC₂-CaF₂ fluxes are shown, and the importance of the post-treatment of spent fluxes is pointed out for environmental reasons.

Any dephosphorization step must satisfy the requirements of present processes for the production of stainless steel in terms of the carbon and chromium contents. The most efficient way of producing stainless steels of low phosphorus content is proposed.

Introduction

It is well known that the resistance to stress-corrosion of austenitic stainless steels is markedly improved by lower phosphorus contents. For example, the time to failure of 20Cr-20Ni steels in a boiling MgCl₂ solution at 143°C, subjected to a stress of 30 kg/mm², is increased from 5 hours to 250 hours by a decrease in the phosphorus content from 0,03 to 0,003 per cent. This improvement in stress-corrosion resistance is the main impetus behind the development of a novel process for the removal of phosphorus from stainless steels.

Conventional dephosphorization of steels has been based on the oxidation of phosphorus, followed by the absorption of the product in suitable slags. However, this principle cannot be applied to the refining of stainless steel because chromium is oxidized in preference to phosphorus, so that a new concept in the physical chemistry of dephosphorization of molten steel had to be developed.

Traditionally, the following techniques have been employed to control the phosphorus content of stainless steels. Firstly, coke with a low phosphorus content should be selected for the reduction of the chromium ore. The specified phosphorus content of stainless steels can be as low as 0,01 per cent. Secondly, low-carbon ferrochromium or electrolytic chromium of low phosphorus content should be used but, if this is done, the production cost is very high. Thirdly, plain carbon steels should be thoroughly dephosphorized before the addition of ferrochromium. The phosphorus content of conventional stainless steels can be controlled at a level of 0,03 per cent by the use of these methods, but it is not possible to achieve a phosphorus content of less than 0,02 per cent in this way.

As described in more detail by Izawa et al. at this meeting, a new smelting-reduction technique has been developed in Japan for the reduction of chromium ore. One of the features of this technique is that coal, rather than electrical power, is used as an energy source for the reduction. The phosphorus content of the metal can be as high as 0,075 per cent if low-grade coal is used. This problem has further motivated the development of a new technique for the removal of phosphorus from chromium steels.

Physicochemical Principles of Dephosphorization

It is well known that phosphorus has two valencies, P⁵⁺ and P³⁻. Figure 1 shows the stabilities of the phosphates and phosphides of calcium and barium as a function of temperature. Since the oxygen partial pressure prevailing in iron- and steel-making is always in the stability area of phosphates, the dephosphorization of steels has traditionally been based on the oxidation of phosphorus according to Equation [1] or [2]:

\[
P + 5 \frac{1}{4} O_2 + \frac{3}{2} O^{2-} = PO_5^{3-} \quad [1] \\
P + \frac{5}{4} O_2 + \frac{1}{2} CaO = \frac{1}{2} Ca_3 (PO_4)_2. \quad [2]
\]

However, as indicated earlier, dephosphorization of chromium steels has necessitated a method not based on oxidation, which has led to the unconventional use of P³⁻. By this technique, phosphorus is removed by reduction to P³⁻.
Suppose molten, carbon-saturated, 13%Cr-Fe \( (a_{Cr} = 0.041) \) is dephosphorized by CaO-saturated slags at 1300°C, the oxygen partial pressure, calculated from Equation [7], is \( 9.5 \times 10^{-17} \) atm. Phosphorus in stainless steels has to be removed at a partial pressure of oxygen below this critical value by the use of highly basic slags.

The ability of a slag to contain phosphorus is expressed by the phosphate capacity, which is defined by reference to Equation [1] as

\[
\log P_{O_2} (\text{atm}) = - \frac{4}{3} \log a_{Cr} + 47,000 \frac{1}{T} + 12.0
\]

When CaO-bearing slags are used, Equation [6], instead of Equation [5], should be considered because of the formation of CaO-Cr2O3:

\[
\frac{4}{3} \text{Cr} + \frac{3}{2} \text{O}_2 + \frac{3}{2} \text{CaO} = \frac{2}{3} \text{CaO}_2 \text{Cr}_2 \text{O}_3 \]  

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\[
C_{P_{O_2}} = \left( \frac{\%P_{O_2}}{P_{O_2}} \right)^{3/2} \frac{1}{f_{P_{O_2}}} \frac{1}{f_{P_2O_3}}
\]

where \( a_{O_2} \) is the activity of free oxide ions and can be regarded as a measure of the basicity of the slag; \( f_{P_{O_2}} \) is the activity coefficient of \( P_{O_2} \) and depends on the slag composition; and \( K_f \) is the equilibrium constant of Equation [1] and increases as the temperature is lowered. Equation [8] indicates that \( C_{P_{O_2}} \) is increased as \( a_{O_2} \), or the slag basicity, is increased.

Traditionally, dephosphorization has been expressed by Equation [9] using molecular formalism:

\[
2P + \frac{3}{2} O_2 = P_2O_3
\]

By definition, \( C_{P_{O_2}} \) is inversely proportional to the square root of \( P_{O_2} \) and the activity coefficient of \( P_{O_2} \).

Generally speaking, slags having larger phosphate capacities are more effective for dephosphorization. Figure 3 shows the phosphate capacities of a variety of basic slags, which were determined experimentally by the present authors. BaO-bearing slags clearly have larger \( C_{P_{O_2}} \) values than CaO-bearing slags, and the temperature dependence of \( C_{P_{O_2}} \) is fairly significant.
According to Figure 3, BaO–BaF₂, Na₂O–SiO₂, and CaO–SiO₂–CaF₂–Na₂O systems are candidate slags for the successful dephosphorization of stainless steels. Figure 5 shows that a small addition of Na₂O to the CaO–SiO₂–CaF₂ slag has a significant effect on dephosphorization. With an Na₂O addition of 3 per cent, the log L̄p is expected to be as high as 200 for carbon-saturated 16%Cr iron at 1300°C at an oxygen partial pressure of 2.7 x 10⁻¹⁷ atm. Although some oxidation of chromium is unavoidable, the chromium oxide content of the slag should be kept as low as possible. Figure 6 shows the solubility of Cr₂O₃ in a CaO–Cr₂O₃ melt at 1500°C. The Cr₂O₃ content at a double saturation of CaO and CaO·Cr₂O₃ is approximately 2 per cent. The value of L̄p at this slag

Figure 4 shows the phosphorus partition ratio, L̄p, between CaO–CaF₂–SiO₂ melts doubly saturated with CaO and 3CaO·SiO₂ with a phosphate capacity of 10²⁻²⁷, and carbon-saturated iron as a function of the chromium content. The solid line with solid circles applies to the case of 1 atm of P₂O₅, indicating that the L̄p decreases with increasing chromium content because of a negative value of e₉P₅. The solid curve shows the calculated L̄p subject to the condition that the partial pressure of oxygen is controlled by Equation [6]. Since the phosphate capacity of this slag is not large enough, the L̄p value for a 16%Cr–C Fe alloy is too low for practical dephosphorization, suggesting the need for a slag with a higher phosphate capacity. The dotted line refers to a conceptual slag with a phosphate capacity of 10²⁻⁷. Such a slag possesses a sufficiently high phosphate capacity for the efficient removal of phosphorus, as indicated by the phosphorus-distribution ratio, L̄p.
TABLE I
CONDITIONS FOR THE DEPHOSPHORIZATION OF Fe-Cr-Cr MELTS BY
THE INJECTION OF CaO-CaF$_2$ FLUXES

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemical compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Cr] = 8–28%</td>
</tr>
<tr>
<td></td>
<td>[P] = [S] = 0,040 %</td>
</tr>
<tr>
<td></td>
<td>[C] = 6 %, [Si] = tr</td>
</tr>
<tr>
<td>Flux</td>
<td>CaO-CaF$_2$</td>
</tr>
<tr>
<td></td>
<td>CaO/CaF$_2$ = 7/3-4/6</td>
</tr>
<tr>
<td>Injection feed rates</td>
<td>Flux: = 1,5 kg/min</td>
</tr>
<tr>
<td></td>
<td>O$_2$ = 60–175 Nl/min</td>
</tr>
<tr>
<td></td>
<td>(O$_2$/Ar=2/1)</td>
</tr>
<tr>
<td>Temperature</td>
<td>1470–1500°C</td>
</tr>
</tbody>
</table>

composition obtained by flux injection – described in detail in Figure 7 – is in excellent agreement with the thermodynamic estimation based on Equation [7] and the C$_{po}$ value for the CaO-CaF$_2$ system shown in Figure 3.

The oxidant for the removal of phosphorus with CaO-CaF$_2$ slags is usually chromium ore. If Ca-CrO$_3$ is used instead, the performance is improved, indicating that dephosphorization proceeds preferentially to chromium oxidation. The recovery of phosphorus occurs towards the end of the treatment as a result of the attainment of equilibrium for both chromium and phosphorus between the metal and the slag. Accordingly, the injection of slag may be effective in that a fresh slag is supplied continuously. For example, CaO-CaF$_2$ slags were injected into 300 kg of an Fe-Cr-C melt with an O$_2$-Ar mixture as the carrier gas, yielding good dephosphorization, as shown in Figure 8 and Table I.

Barium oxide is more basic than CaO so that an improvement in dephosphorization is expected from its addition to CaO-bearing slags, as shown in Figure 9.

Figure 10 shows the activity of P$_2$O$_5$ in the BaO-BaF$_2$-BaCl$_2$-CaO system. BaF$_2$ and CaO are more effective than CaCl$_2$ and CaO, respectively. However, if the slag is kept saturated with CaO when BaO is replaced by CaO, the dephosphorization capability will not deteriorate, as expected from the recent measurement by the authors of the sulphide capacity of the BaO-BaF$_2$-CaO saturated system.

Figures 11 and 12 show thermodynamic and kinetic aspects in the dephosphorization of Fe-Cr-C melts by the BaO-BaF$_2$ system. The BaO-BaCl$_2$ flux has been used in practice to dephosphorize crude stainless steels. Although
relatively large consumption of flux is needed, efficient
dephosphorization at low carbon content (1 to 2 per cent)
and high chromium content (up to 25 per cent) was attained
by strong agitation of the metal bath in an AOD vessel.

Alkaline metal oxide is highly basic and is expected to be
an efficient additive to CaO-bearing slags, as described
earlier with reference to the Na₂O additions in Figure 5.
However, Na₂O is too basic in the sense that it is easily
reduced by co-existing chromium or carbon to form sodium
vapour before reacting with the phosphorus. Therefore,
thermodynamically, Li₂O is a more realistic additive
because it is less basic than Na₂O.
Figure 13 shows the results of dephosphorization of \( \text{Fe-Cr} \) melts by a \( 1\% \text{Li}_2\text{CO}_3-14\% \text{CaO} -47\% \text{CaF}_2-29\% \text{FeO} \) slag. For an \( 18\% \text{Cr}-6\% \text{C}-\text{Fe} \) alloy, 60 per cent of the phosphorus was removed by the use of 70 kg/t of this flux. The \( \text{Na}_2\text{SiO}_3-\text{NaF} \), \( \text{Na}_2\text{CO}_3-\text{NaCl} \), \( \text{CaCl}_2 \), \( \text{FeCl}_2 \), \( \text{K}_2\text{CO}_3-\text{KCl} \), and KF systems have been evaluated extensively for the removal of 60 to 80 per cent of the phosphorus. A typical example of dephosphorization by an \( \text{Na}_2\text{SiO}_3-\text{NaF} \) flux is shown in Figure 14. The major disadvantage of these fluxes is their high cost.

Slags used for dephosphorization by oxidation are a combination of oxides (\( \text{CaO} \), \( \text{BaO} \), \( \text{NaO}_2 \), \( \text{Li}_2\text{O} \) etc.), halides (\( \text{CaF}_2 \), \( \text{CaCl}_2 \), \( \text{BaCl}_2 \), \( \text{BaF}_2 \), \( \text{NaF} \), etc.), and oxidants (\( \text{Cr}_2\text{O}_3 \), \( \text{CaCr}_2\text{O}_4 \), \( \text{Fe}_2\text{O}_3 \), etc.). The functions of the halides are to lower the melting point of the slag and the activity coefficient of \( \text{P}_2\text{O}_5 \), and to raise the activity coefficient of \( \text{Cr}_2\text{O}_3 \).

The reasons for the recent success of the dephosphorization of stainless steels by oxidation is as follows. Firstly, the carbon content is increased to between 2 and 4 per cent, corresponding to the metal composition prior to being charged to an AOD furnace, resulting in less oxidation of chromium and an increased activity coefficient of phosphorus. Secondly, highly basic oxides such as \( \text{BaO} \) and \( \text{Na}_2\text{O} \) are used. Thirdly, some halides are added. The key to further success would be to avoid the contamination of the slags by refractory materials such as \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \), and to keep the temperature at which the treatment is done as low as possible.

**Dephosphorization by the Reduction of Phosphide**

In the application of Equation [3] in practice, molten calcium and \( \text{CaC}_2-(\text{CaF})_2 \) fluxes have been used to keep the partial pressure of oxygen sufficiently low, as expressed by Equations [10] and [11]:

\[
\text{Ca(1)} + \frac{1}{2} \text{O}_2 = \text{CaO} \quad [10]
\]

\[
\text{CaC}_2 + \frac{1}{2} \text{O}_2 = \text{CaO} + 2\text{C} \quad [11]
\]

Accordingly, Equation [3] can be rewritten

\[
\frac{3}{2} \text{Ca} + \text{P} = \frac{3}{2} \text{Ca}^{2+} + \text{P}^{3-} \quad [12]
\]

Figure 15 shows the phosphorus content of molten iron as a function of its calcium content for various fluxes at 1600°C, satisfying the relationship expected by Equation [12].

A pioneering test was successfully carried out by Nakamura et al., who employed an ESR technique in the remelting of stainless steels using a \( \text{Ca-CaF}_2 \) flux, which lowered the vapour pressure of calcium.
In practice, CaC$_2$ has been used instead of calcium for economic reasons. Figure 16 shows the removal of phosphorus, sulphur, and nitrogen, and the build-up of carbon in crude stainless steels. The calcium content of the CaC$_2$-CaF$_2$ melt increased as the CaC$_2$ dissociated and then decreased as a result of the oxidation of impurities or evaporation.

The results of an industrial-scale trial are shown in Figure 17. Figure 18 shows the effect of the carbon content of the metal on dephosphorization. As expected from Equation [11] and shown in Figure 17, dephosphorization is decreased as the carbon content of the metal is increased. The function of CaF$_2$ is to dissolve the CaC$_2$ so as to maintain a molten flux and to dissolve the calcium as a dissociation product of CaC$_2$, thereby avoiding its violent

**TABLE II**

<table>
<thead>
<tr>
<th>Electrode Position* mm</th>
<th>Transition element, %</th>
<th>I-b</th>
<th>II-b</th>
<th>III-b</th>
<th>IV-b group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
<td>Mn</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
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<tr>
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<tr>
<td>Heat 1</td>
<td></td>
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<td></td>
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<tr>
<td>30</td>
<td>17.03</td>
<td>1.30</td>
<td>7.80</td>
<td>770</td>
<td>84</td>
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<td>120</td>
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<tr>
<td>210</td>
<td>17.08</td>
<td>1.30</td>
<td>7.74</td>
<td>710</td>
<td>77</td>
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<tr>
<td>Heat 2</td>
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<td></td>
</tr>
<tr>
<td>30</td>
<td>17.08</td>
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<td>7.78</td>
<td>770</td>
<td>73</td>
</tr>
<tr>
<td>120</td>
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<tr>
<td>210</td>
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</tbody>
</table>

* Distance measured from the ingot bottom

DEPHOSPHORIZATION OF STAINLESS STEELS
Although the dephosphorization of stainless steels was considered to be impossible in the past, it has been achieved in the past decade by the adoption of new physicochemical concepts. In the assessment of various techniques of dephosphorization, it is very important for one to determine whether the metal composition satisfies the requirements for the conventional stainless-steelmaking processes. Figure 21 is a summary of the various techniques in terms of carbon and chromium contents, and the optional products of the three stages of dephosphorization are apparent:

1. high-carbon ferrochromium,
2. medium-carbon stainless steels before decarburization
3. low-carbon stainless steels before casting.

It has not been found possible to dephosphorize ferrochromium. The second possibility may be an option by the use of BaO or modified CaO-bearing slags for the oxidation of phosphorus. Alternatively, CaC2–CaF2 fluxes can be used under reducing conditions, and can be applied to high-chromium metal, followed by mixing with low-

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**Summary**

Although the dephosphorization of stainless steels was considered to be impossible in the past, it has been achieved in the past decade by the adoption of new physicochemical concepts. In the assessment of various techniques of dephosphorization, it is very important for one to determine whether the metal composition satisfies the requirements for the conventional stainless-steelmaking processes. Figure 21 is a summary of the various techniques in terms of carbon and chromium contents, and the optional products of the three stages of dephosphorization are apparent:

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**Figure 17.** Dephosphorization with CaC2–CaF2 flux in a plant

**Figure 18.** Influence of the activity of carbon in the metal on the dephosphorization (plots: experiment with 50 per cent CaC2–50%CaF2 flux in a rotating crucible)

**Figure 19.** Influence of (%CaF2) on the decomposition of CaC2 and on the degree of dephosphorization in experiments of 600 kg scale with the top addition of flux

**Figure 20.** Results of oxygen blowing
FIGURE 21. Suitable metal compositions for various methods of dephosphorization.

carbon steels. The third case may be realized only by the use of Ca–CaF₂ fluxes.

In conclusion, it is believed that, for economic reasons, the most realistic approach is to dephosphorize crude stainless steels containing approximately 2 per cent carbon, which are supplied to the AOD process, by the use of CaO-bearing slags and some efficient additives such as Na₂O, BaO, etc. At the same time, the oxidation loss of chromium must be contained.

References